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Concentrations of ultrafine, fine and $PM_{2.5}$ particles in three European cities☆

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Abstract

Total number concentrations, number concentrations of ultrafine (0.01–0.1 μm) and accumulation (0.1–0.5 μm) particles, as well as mass concentration of $PM_{2.5}$ particles and blackness of $PM_{2.5}$ filters, which is related to Black Smoke were simultaneously monitored in three European cities during the winter period for three and a half months. The purpose of the study was to describe the differences in concentration levels and daily and diurnal variations in particle number and mass concentrations between European cities. The results show statistically significant differences in the concentrations of $PM_{2.5}$ and the blackness of the $PM_{2.5}$ filters between the cities, but not in the concentrations of ultrafine particles. Daily $PM_{2.5}$ levels were found to be poorly correlated with the daily total and ultrafine number concentrations but better correlated with the number concentration of accumulation particles. According to the principal component analysis airborne particulate pollutants seem to be divided into two major source categories, one identified with particle number concentrations and the other related to mass-based information. The present results underline the importance of using both particle number and mass concentrations to evaluate urban air quality.

Keywords: Ultrafine particles; Fine particles; $PM_{2.5}$; Urban air quality; Black smoke

1. Introduction

Recent concern with the health effects of air pollution has focused on particulate matter as several epidemiological studies have shown a strong link between increased PM_{10} concentrations and increased mortality, morbidity and respiratory symptoms (Dockery and Pope., 1994; Pope et al., 1995a, b; Brunekreef et al., 1995). In the search for associations between cardiorespiratory health and urban air particles, a large number of fine and

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ultrafine particles has been proposed as a major factor contributing to such health effects (Seaton et al., 1995). Oberdörster et al. (1994) showed that a high number concentration of ultrafine particles ($<0.1\,\mu m$ in diameter) may cause serious health effects in rats even if their mass concentrations are very low. An association between ultrafine and fine particles and respiratory health has recently been found in asthmatic adults and children (Peters et al., 1997; Pekkanen et al., 1997). Number concentrations of ultrafine particles were shown by Peters et al. (1997) to be more closely associated with variations in lung function than PM_{10} or fine particles. Pekkanen et al. (1997) demonstrated equally strong effects for both ultrafine and PM_{10} particles. Ultrafine particles have a relatively high deposition rate in the lungs and they are also able to penetrate into the interstitial space.

The urban air particles are complex mixtures of solid and liquid material emitted from different sources, and often divided into coarse particles (CP, of diameter larger than 2.5 μm) and fine particles ($PM_{2.5}$, mass concentration of diameter smaller than 2.5 μm). In the atmosphere particles are typically distributed into three modes according to their mechanisms of formation. Fine particles are often subdivided roughly into two size classes, of which the range from 0.01 to 0.1 μm in diameter is known as the ultrafine or nuclei mode which is emitted particularly from combustion processes or formed in homogeneous nucleation of supersaturated vapours. The characteristic of these particles is their high number per unit of air volume and they account for preponderance of the number of all urban air particles.

Although these can be hundreds of thousands of ultrafine particles in a cubic centimetre of urban air, they still account for a negligible fraction of the total mass concentration. Therefore, the present mass-based air quality standards cannot be applied to describe the levels of ultrafine particles.

The rough size range 0.1–1 μm is known as the accumulation mode, the particles being formed by coagulation of ultrafine particles and condensation of gases and vapours onto pre-existing particles of both modes. The lower end of the accumulation mode usually accounts for most of the surface area of particles and the upper end for a substantial part of particle mass. Accumulation particles are in general too small to be removed by gravity and too large to coagulate into larger particles, so that their atmospheric lifetimes are in the order of a few days and even longer.

Since little work has been done to monitor the number and size distributions of particles in urban air, we describe here a measurement campaign aimed at monitoring simultaneously both number concentrations of ultrafine and accumulation particles and mass concentrations of $PM_{2.5}$ particles at urban background sites. The purpose was to describe differences in particle number and mass concentrations between three European cities, and to describe daily and diurnal variations in particle number and mass concentrations.

2. Methods

2.1. Site details

The quality of the ambient air in three European cities was monitored between 30 November 1996 and 13 March 1997. The cities selected were Alkmaar in the Netherlands, Erfurt in Germany, and Helsinki in Finland. The measurements were performed at one location representing urban background levels of air pollution.

The city of Alkmaar is located in the northern part of the Netherlands, less than 10 km from the coast of the North Sea. The monitoring site was about 1.5 km south of the city centre and more than 100 m away from major streets. The city of Erfurt is located in a valley surrounded by mountains of the Thuringer Wald. The monitoring site was about 1 km to the south of the city centre and more than 40 m away from any major streets. Helsinki is situated by the Baltic Sea, and the centre of the city is on a peninsula. The monitoring site was in a park about 2 km northeast of the city centre, and more than 50 m from any major streets. The inlets of the instruments were at a height of 4 m above the ground. Pronounced inversion conditions occur frequently in winter in both Erfurt and Helsinki, giving rise to episodes of high pollution.

2.2. Instrumentation

Three aerosol spectrometers were used to monitor the number concentrations of urban air particles and their size distribution. These spectrometers measured the number distribution of particles every 10 min or less, and then these values were used to calculate 1 and 24 h averages if there was not more than 33% of missing values in the noon to noon measurement period. Two discrete size ranges were selected, $0.01\,\mu m \leqslant d \leqslant 0.1\,\mu m$ for ultrafine particles and $0.1\,\mu m \leqslant d \leqslant 0.5\,\mu m$ for accumulation particles. The number concentrations of particles in these size ranges were denoted as $NC_{0.01-0.1}$ and $NC_{0.1-0.5}$, respectively.

In Erfurt the mobile aerosol spectrometer (MAS) was used, as described in detail earlier (Brand et al., 1991; Brand and Ruoss, 1992; Tuch et al., 1997). It consists of two commercially available instruments covering partly overlapping size ranges. Particles in the size range from 0.01 to 0.5 μm are measured using a differential mobility analyser (DMA, TSI model 3071) combined with a condensation particle counter (CPC, TSI model 3760). Particles in the size range from 0.1 up to 2.5 μm are classified by an optical laser aerosol spectrometer (PMS model LAS-X). The spectrometer used in Alkmaar

(denoted as DAS) was similar to MAS but consisted of a scanning mobility particle analyser (SMPS) (SMPS, TSI) and an optical laser aerosol spectrometer (PMS LAS-X). The SMPS, which employs the same principle to measure the concentration of aerosol particles as a function of size as does the DMPS in the MAS, consists of an electrostatic classifier (EC-3071, TSI) and a CPC (CPC-3010, TSI) but differs from the DMPS in the MAS in that the voltage used to select particle fractions of equal electrical mobility is not changed in discrete steps but is scanned continuously. The third spectrometer, used in Helsinki, was an electrical aerosol spectrometer (EAS). It measures the particle size distribution in the size range 0.01–10 μm by an electrical method alone (Kikas et al., 1996), employing unipolar diffusion charging in the size range 0.01–0.5 μm in one analyzer and strong electrical field charging in the range 0.3–10 μm in the other, each made up of a series of electrometers determining the charge of particles of equal electrical mobility. Interference between particles of different sizes is corrected for mathematically (Mirme, 1994).

Total number concentrations of particles were monitored in each city using condensation particle counters (model CPC3022A, TSI) as integral counting instruments. These counters can monitor particles larger than 0.02 μm in diameter, but having still 50% counting efficiency at 0.007 μm. The quality of the data given by all the CPCs was determined by the factory calibration and operation procedures provided by the manufacture.

Harvard impactor $PM_{2.5}$ samplers (Air Diagnostic and Engineering, Inc.) were used to obtain mass-based information on fine particles. Twenty-four-hour samples taken from noon to noon were collected. The impactors were similar to the one described by Marple et al. (1987), except that the latter had only one impaction stage. The inlet was designed to sample particles of 2.5 μm with an efficiency of 50% at a flow rate of $10\,l\,min^{-1}$ ($4\,l\,min^{-1}$ in the older model used in Erfurt). A glass critical orifice was used to provide constant flows. Teflon filters with a polymethylpentene support ring and 2 μm pore size (Gelman Sciences) were used. The filter type used should have a collection efficiency of at least 99% for 0.3 μm particles. The low chemical background, low-pressure drop during sampling and excellent aerosol retention ability were the properties which made it the best choice for the present purpose.

Blackness of the $PM_{2.5}$ filters was also measured. The reflectance measurements of collected $PM_{2.5}$ filters were performed using two smoke stain reflectometers (EEL43 Diffusion System Limited, London, UK) consisting of a light source and a detector unit. The $PM_{2.5}$ filters used in Alkmaar and Erfurt were processed at the University of Wageningen in the Netherlands, and those collected in Helsinki at National Public Health Institute, Finland. The instruments employ white light and have a digital readout of percentage reflectance on a linear scale (0–100%). They were calibrated with a pre-selected clean control filter taken from the same batch as the sampling filters and with two standard samples (100%, 33%) supplied by the manufacturer. Calibration was repeated after every ten sample filters during the measurements to ensure comparable and reproducible results. The ISO 9835 standard "Ambient air – Determination of a black smoke index" (ISO 9835:1993(E), 1993) was used to calculate the absorption coefficient (denoted as ABS) of the $PM_{2.5}$ filters.

2.3. Quality assurance and control

Quality assurance and control procedures were performed with regard to the aerosol spectrometers, the $PM_{2.5}$ sampling and weighing and the reflectance measurements in order to limit and assess the methodological differences between the measurement methods used in the three cities. As the aerosol spectrometers were based on different measurement principles and there is no standard instrument available for making comparative measurements of the particle fractions of interest, side by side comparison of the three spectrometers was performed prior to the field measurement campaign (Tuch et al., 2000; Mirme et al., 2000). The side by side comparison tests were also made in a laboratory with three different kinds of artificial test aerosols (Khlystov et al., 2000). The results showed that the systematic differences between the instruments were within 10% and the correlation around 0.98 in the particle size range from 0.01 to 0.5 μm. The results suggest that the MAS, DAS and EAS are suitable instruments for reliable characterisation of the number concentrations of ambient particles having sizes smaller than 0.5 μm and their comparison between cities.

A detailed operation procedure was used by the field operators for $PM_{2.5}$ sampling in Alkmaar, Erfurt and Helsinki. Each centre was required to collect at least 10–20 field banks to assess the performance of the sampling methods and a round robin test of the analysis of filter weighing based on 10 sampled filters was included in the quality assurance control for the $PM_{2.5}$ filters. The filters were weighed under standard conditions of temperature ($20 \pm 1°C$) and relative humidity ($40 \pm 5\%$). Estimated errors in $PM_{2.5}$ results due to weighing were $\pm 2.6\,\mu g\,m^{-3}$ in Alkmaar, $\pm 0.5\,\mu g\,m^{-3}$ in Erfurt, and $\pm 0.6\,\mu g\,m^{-3}$ in Helsinki.

In addition, the reflectance measurements were checked by means of a round robin test on two reflectometers. The error of the reflectance measurements was within $\pm 1.0\%$.

2.4. Statistical analysis

Twenty-four average concentrations were found be close to normally distributed and, therefore, *t*-tests for

independent samples were used to test differences between cities. Tests were, however, repeated using nonparametric Mann–Whitney *U*, which is based on comparison between medians rather than means, but the conclusions from these tests were identical to those presented. In contrast, hourly averages have asymmetric distributions and a high number of low-concentration values and therefore geometric averages and geometric standard deviations are reported. All correlations are nonparametric Spearman rank ordered correlations.

Principal component analysis (PCA), a technique which attempts to explain the statistical variance in a given data set, was also used. The purpose of these PCA analyses was to find a minimum number of simple significant underlying (latent) components (factors) in the data sets. PCA has been widely employed to identify possible emission source categories observed at a receptor site. The statistical software package STATISTICA for Windows 5.0 (StatSoft, Inc., 1996, USA) was used for all the statistical calculations.

Diurnal variations in particle number concentrations were examined by averaging all hourly values separately for all weekdays and for the weekend (Saturdays and Sundays) (Figs. 2 and 3).

3. Results

3.1. 24-h averages

Total number concentration (TN) measured by CPC and number concentrations of ultrafine ($NC_{0.01-0.1}$) and accumulation ($NC_{0.1-0.5}$) particles measured by the aerosol spectrometers, as well as mass concentration of $PM_{2.5}$ particles and blackness of $PM_{2.5}$ filters related to Black Smoke (ABS) were simultaneously monitored over the period 30 November 1996 to 13 March 1997 to assess how comparable the levels of particulate matter in the three European cities are. Plots of daily averages of TN, $NC_{0.01-0.1}$ and $PM_{2.5}$ in the three cities are shown in Fig. 1a–c. The results show the great variability in both number and mass concentrations. The behaviour of the elevated $PM_{2.5}$ concentrations features high concentration episodes lasting even six to eight days.

The concentrations of $PM_{2.5}$ and the blackness of the $PM_{2.5}$ filters differed greatly between the cities, being highest in Erfurt and lowest in Helsinki (Table 1). No clear differences were observed in the concentrations of ultrafine particles ($NC_{0.01-0.1}$). On the other hand, total number concentrations and accumulation particles were

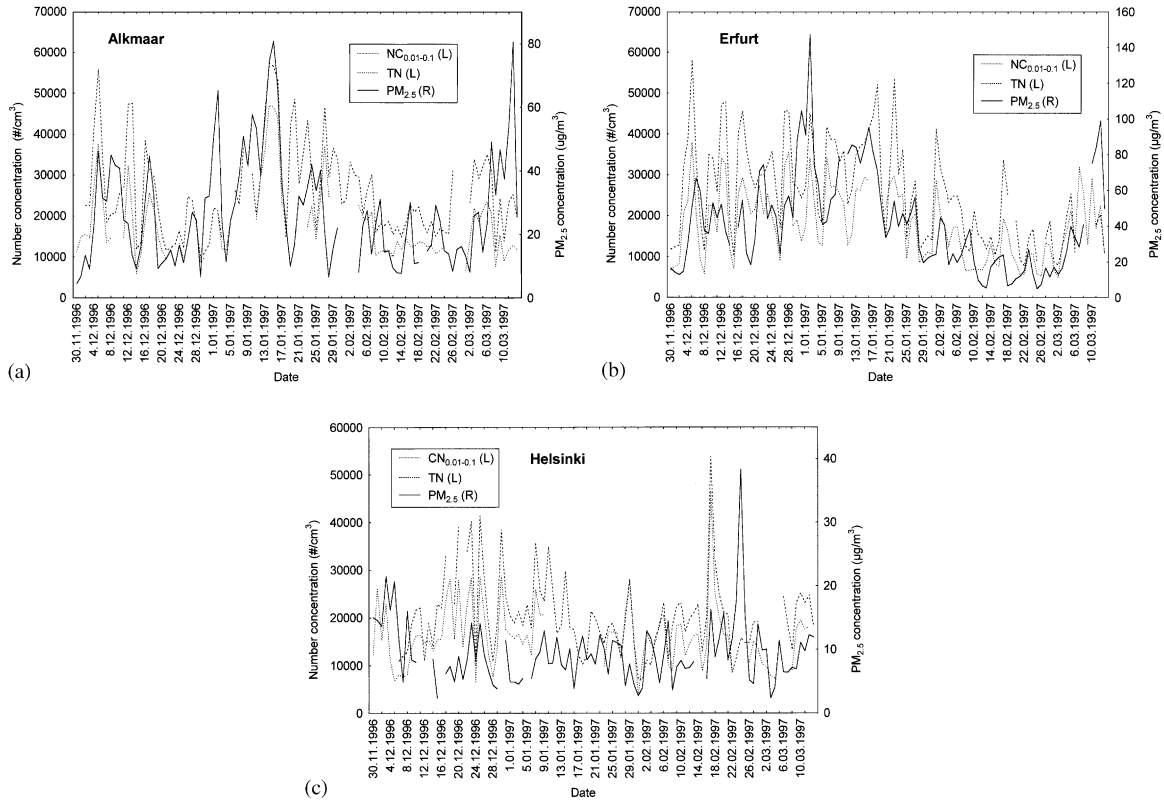

Fig. 1. (a) Time series of number concentration of total and ultrafine particles and mass concentration of $PM_{2.5}$ monitored in Alkmaar. (b) Time series of number concentrations of total and ultrafine particles and mass concentration of $PM_{2.5}$ monitored in Erfurt. (c) Time series of number concentrations of total and ultrafine particles and mass concentration of $PM_{2.5}$ monitored in Helsinki.

Table 1
24 h average concentrations of $NC_{0.01-0.1}$, $NC_{0.1-0.5}$, TN levels (particles cm^{-3}), $PM_{2.5}$ levels ($\mu g\ m^{-3}$) and Blackness of $PM_{2.5}$ filters (ABS) ($10{,}000\ m^{-1}$) during the measurement period 30/11/96–13/3/97

	Valid N	Mean	S.D.	Min	25th Percentile	Median	75th Percentile	Max
Alkmaar								
$NC_{0.01-0.1}$	81	18,300	8910	5870	11800	14900	22,000	47,100
$NC_{0.1-0.5}$	78	2120	1740	306	959	1670	2590	9160
TN	96	25,800	11,300	9700	17,200	23,100	31,200	57,400
$PM_{2.5}$	99	27.0[a]	17.2	4.44	13.9	23.7	35.4	80.7
ABS	103	1.76[a]	0.96	0.54	1.05	1.55	2.28	4.94
Erfurt								
$NC_{0.01-0.1}$	101	17700	8680	4960	10,400	17,000	25,000	38,000
$NC_{0.1-0.5}$	101	2270	1470	291	1140	1870	3170	6700
TN	98	25,900	12,200	7760	14,500	25,300	35,000	58,200
$PM_{2.5}$	101	41.9[a]	27.1	5.06	19.8	38.9	55.0	147
ABS	101	4.00[b]	2.34	0.552	1.89	3.68	5.81	11.1
Helsinki								
$NC_{0.01-0.1}$	85	16,200	6700	3680	12,100	15,600	18,600	46,500
$NC_{0.1-0.5}$	85	973[b]	470	129	649	905	1200	2390
TN	92	20,300[b]	8200	7110	14,800	18,900	23,100	53,800
$PM_{2.5}$	97	9.42[a]	4.99	2.37	6.28	8.45	11.7	38.3
ABS	96	1.42[a]	0.57	0.26	1.05	1.26	1.71	3.00

[a]All comparisons between the three cities are significant ($p < 0.05$).
[b]Significantly different from both Alkmaar and Erfurt ($p < 0.01$).

observed to differ statistically significantly between Helsinki and the other cities but not between Alkmaar and Erfurt.

Variations in the parameters measured can be examined mathematically by comparing the coefficients of variation (CV; standard deviation divided by the mean). $PM_{2.5}$ particles showed significant variability in all three cities, with CVs ranging from 53% in Helsinki to 65% in Erfurt, while total number concentrations were found to have the lowest variability, with CVs between 40 and 47%. The highest variability of all was for accumulation particles in Alkmaar 82% when the respective variability was 65% in Erfurt and 48% in Helsinki. The variability of the parameters was generally lower in Helsinki than in either Erfurt or Alkmaar.

The concentrations of ultrafine particles ($NC_{0.01-0.1}$ and TN) differed statistically significantly between weekdays and weekends in all cities (Table 2), whereas no difference was observed in the concentrations of $NC_{0.1-0.5}$, $PM_{2.5}$ or blackness of $PM_{2.5}$ filters.

The correlation between the concentrations measured at each site showed great similarities (Table 3). In general, the highest correlations of $PM_{2.5}$ with other measurements were observed in Erfurt. The number concentration of ultrafine particles and $PM_{2.5}$ were not closely correlated (0.23–0.61). TN was not at all correlated with $PM_{2.5}$ in Helsinki. The blackness of the $PM_{2.5}$ filters correlated better with the number concentration of

Table 2
Differences between weekdays and weekends in median levels of 24 h average concentrations (dimensions as in Table 1)

	Mean (Weekdays)	Mean (Saturday)	Mean (Sunday)
Alkmaar			
$NC_{0.01-0.1}$	18,900	12,200[a]	16,800
$NC_{0.1-0.5}$	1850	2050	1730
TN	26,000	16,300[a]	22,700
$PM_{2.5}$	26.9	22.7	24.5
ABS	2.50	1.35[b]	1.40
Erfurt			
$NC_{0.01-0.1}$	19,300	14,900	12,000[c]
$NC_{0.1-0.5}$	2660	2250	2340
TN	27,900	22,500	18,900[c]
$PM_{2.5}$	41.8	42.5	41.5
ABS	4.09	4.07	3.53
Helsinki			
$NC_{0.01-0.1}$	17,300	10,900[a]	16,400
$NC_{0.1-0.5}$	1020	820[b]	900
TN	21,700	14,200[a]	18,700
$PM_{2.5}$	9.63	8.00	9.80
ABS	1.48	1.27	1.29

[a]$p < 0.001$.
[b]$p < 0.05$.
[c]$p < 0.01$.

Table 3
Spearman rank order correlations of 24 h average concentrations

	$NC_{0.1-0.5}$	TN	$PM_{2.5}$	ABS
Alkmaar				
$NC_{0.01-0.1}$	0.459[a]	0.904[a]	0.358[b]	0.659[a]
	$N = 81$	$N = 65$	$N = 75$	$N = 79$
$NC_{0.1-0.5}$		0.414[a]	0.689[a]	0.730[a]
		$N = 72$	$N = 76$	$N = 77$
TN			0.322[b]	0.623[a]
			$N = 91$	$N = 95$
$PM_{2.5}$				0.753[a]
				$N = 98$
Erfurt				
$NC_{0.01-0.1}$	0.628[a]	0.930[a]	0.614[a]	0.650[a]
	$N = 101$	$N = 95$	$N = 98$	$N = 98$
$NC_{0.1-0.5}$		0.630[a]	0.897[a]	0.870[a]
		$N = 95$	$N = 98$	$N = 98$
TN			0.586[a]	0.673[a]
			$N = 96$	$N = 96$
$PM_{2.5}$				0.851[a]
				$N = 98$
Helsinki				
$NC_{0.01-0.1}$	0.625[a]	0.848[a]	0.233[c]	0.645[a]
	$N = 87$	$N = 74$	$N = 78$	$N = 77$
$NC_{0.1-0.5}$		0.582[a]	0.798[a]	0.832[a]
		$N = 74$	$N = 78$	$N = 77$
TN			0.049	0.565[a]
			$N = 85$	$N = 84$
$PM_{2.5}$				0.552[a]
				$N = 96$

[a] $p < 0.001$.
[b] $p < 0.01$.
[c] $p < 0.05$.

accumulation particles than with the mass of $PM_{2.5}$ particles, which can be partly composed of soil particles mechanically generated by traffic.

The PCA loadings of the variables, eigenvalues of the PC factors and percentages of total variance of the data set explained are presented in Table 4 for both the particle and meteorological data. The data for each city yielded four principal components (factors) with the eigenvalues greater than 1, explaining 91.7% of the total variance in Alkmaar, 92.9% in Erfurt and 90.2% in Helsinki. The values for the respective loadings presented in Table 4, provide a reasonable interpretations for these four components. Only the loadings close to 70% of the maximum values are selected as significant in the PC interpretation. In all cities, the different factors can been interpreted to represent mainly either $PM_{2.5}$, ultrafine particles, temperature, or relative humidity. The first factor ('$PM_{2.5}$') in Erfurt and Helsinki is a measure of accumulation and $PM_{2.5}$ particles, and the blackness of the $PM_{2.5}$ filters, explaining 32–34% of the total variance in the data sets, whereas in Alkmaar the '$PM_{2.5}$' factor is the factor 4, which accounts for 23% of the total variance, a much lower proportion than in Erfurt and Helsinki. However, in Alkmaar accumulation particles and the blackness of the $PM_{2.5}$ filters have also high loadings in the 'ultrafine' factor, which in Alkmaar is the first factor and mainly related to the number concentrations of $NC_{0.01-0.1}$ and TN particles. The main contributors to factor 2 in Erfurt and Helsinki are likewise the number concentrations of $NC_{0.01-0.1}$ and TN particles, explaining 26–28% of the total variance, in contrast to 35% in Alkmaar. Temperature and relative humidity explain between 12 and 23% of total variance. Wind speed loads to different factors in different cities, but has consistently an inverse effect on number concentrations, particularly in Helsinki.

3.2. Diurnal variations

Only the data on the variables $NC_{0.01-0.1}$, $NC_{0.1-0.5}$ and TN, the statistical characteristics of which are presented in Table 5, were available for on hours analyses. The results show that TN reached hourly maximum values of up to 188,000 cm^{-3} on weekdays, and that the peak values were about 60 and 30% higher in Erfurt than in Alkmaar or Helsinki, respectively. Little difference was observed between cities in maximum concentrations of $NC_{0.01-0.1}$. Highest concentrations were observed during weekdays in all cities (data not shown). The hourly averages for number concentrations were notably more variable than the daily averages, CVs for ultrafine particles being between 74 and 84%, and for accumulation particles between 75 and 92%. The variability was again lowest in the total number concentration of particles, the CVs being between 71 and 79%.

Diurnal variations in total and ultrafine number concentrations on weekdays as Box–Whiskers presentation are shown in Fig. 2 for Erfurt. The periods with high concentrations are related to particle emissions from traffic during the rush-hours when people are driving to and from work. This is particularly true for the ultrafine particles, were as the concentration recorded at night are more or less constant at one-twentieth of the peak levels. Accumulation particles behaved quite differently, however, as they were distributed more evenly over the weekdays than ultrafine particles and no increase could be observed at rush-hours. Number concentrations followed a different diurnal rhythm at weekends (Fig. 3) in Erfurt. The diurnal behaviour of the ultrafine number concentration was quite different from that of the total number concentration. One explanation would be secondary aerosol formation which could be observed in the total number concentrations due to the lower cutoff size (2 nm) of the used CPC instrument compared with the EAS (10 nm). This explanation is supported by the results of Väkevä et al. (1999) measured in urban environment.

Table 4
Factor loadings (Varimax normalised) of 24 hour samples in Alkmaar, Erfurt and Helsinki

Alkmaar	Factor 1 (Ultrafines)	Factor 2 (Temperature)	Factor 3 (Humidity)	Factor 4 ($PM_{2.5}$)
$NC_{0.01-0.1}$	0.929	− 0.056	0.114	0.274
$NC_{0.1-0.5}$	0.644	− 0.224	− 0.006	0.626
TN	0.933	0.094	0.155	0.261
$PM_{2.5}$	0.283	− 0.068	0.104	0.915
ABS	0.648	− 0.133	0.172	0.663
Wind speed	− 0.367	0.283	− 0.826	− 0.061
Relative humidity	− 0.081	0.513	0.777	0.132
Temperature	0.001	0.947	− 0.004	− 0.163
Eigenvalue	2.79	1.32	1.36	1.86
% of total variance	34.9	16.6	17.0	23.2
Erfurt	Factor 1 (PM2.5)	Factor 2 (Ultrafines)	Factor 3 (Temperature)	Factor 4 (Humidity)
$NC_{0.01-0.1}$	0.287	0.898	0.226	0.133
$NC_{0.1-0.5}$	0.853	0.314	0.173	0.227
TN	0.283	0.914	0.196	0.138
$PM_{2.5}$	0.850	0.189	0.224	0.299
ABS	0.813	0.350	0.344	0.094
Wind speed	− 0.297	− 0.371	− 0.814	− 0.045
Relative humidity	− 0.434	− 0.228	− 0.317	− 0.802
Temperature	0.211	0.112	0.876	0.305
Eigenvalue	2.59	2.10	1.82	0.93
% of total variance	32.4	26.3	22.7	11.5
Helsinki	Factor 1 ($PM_{2.5}$)	Factor 2 (Ultrafines)	Factor 3 (Temperature)	Factor 4 (Humidity)
$NC_{0.01-0.1}$	0.588	0.705	− 0.200	0.135
$NC_{0.1-0.5}$	0.855	0.433	0.054	0.102
TN	0.469	0.733	− 0.192	0.209
$PM_{2.5}$	0.926	− 0.102	0.140	− 0.063
ABS	0.767	0.498	0.032	0.225
Wind speed	0.037	− 0.831	− 0.232	− 0.284
Relative humidity	0.108	0.019	0.963	− 0.045
Temperature	− 0.079	− 0.285	0.056	− 0.951
Eigenvalue	2.76	2.25	1.08	1.11
% of total variance	34.5	28.2	13.6	13.9

Similar behaviour was also observed in Alkmaar and Helsinki (data not shown).

4. Discussion

Twenty-four-hour concentrations of the $PM_{2.5}$ particle fraction differed between the three cities, being highest in Erfurt and lowest in Helsinki. No such difference was observed in the concentration of ultrafine particles. Compared with other $PM_{2.5}$ studies, the levels recorded in Alkmaar and Erfurt were quite similar to those measured elsewhere (Wilson and Suh, 1997; Harrison et al., 1997; Ostro et al., 1991; Neas et al., 1996), whereas those measured in Helsinki were significantly lower. Variability of $PM_{2.5}$ was also the lowest in Helsinki.

Daily $PM_{2.5}$ was found to be poorly correlated with daily total and ultrafine number concentrations but

Table 5
Statistical characteristics of one hour averages of particle number concentrations (particles cm^{-3})

	Valid N	Mean	Median	Minimum	Maximum	S.D.
Alkmaar						
$NC_{0.01-0.1}$	1877	18,400	14,800	1190	115,000	13,700
$NC_{0.1-0.5}$	1786	2080	1500	138	15,100	1900
TN	2256	26,000	21,100	2890	118,000	17,700
Erfurt						
$NC_{0.01-0.1}$	2384	17,700	13,800	726	129,000	13,600
$NC_{0.1-0.5}$	2384	2310	1790	109	10,800	1740
TN	1938	26,200	20,900	900	18,8000	18,500
Helsinki						
$NC_{0.01-0.1}$	2031	16,600	12,300	892	124,000	14,000
$NC_{0.1-0.5}$	2031	980	770	30	7910	797
TN	2202	20,500	16,300	691	145,000	16,100

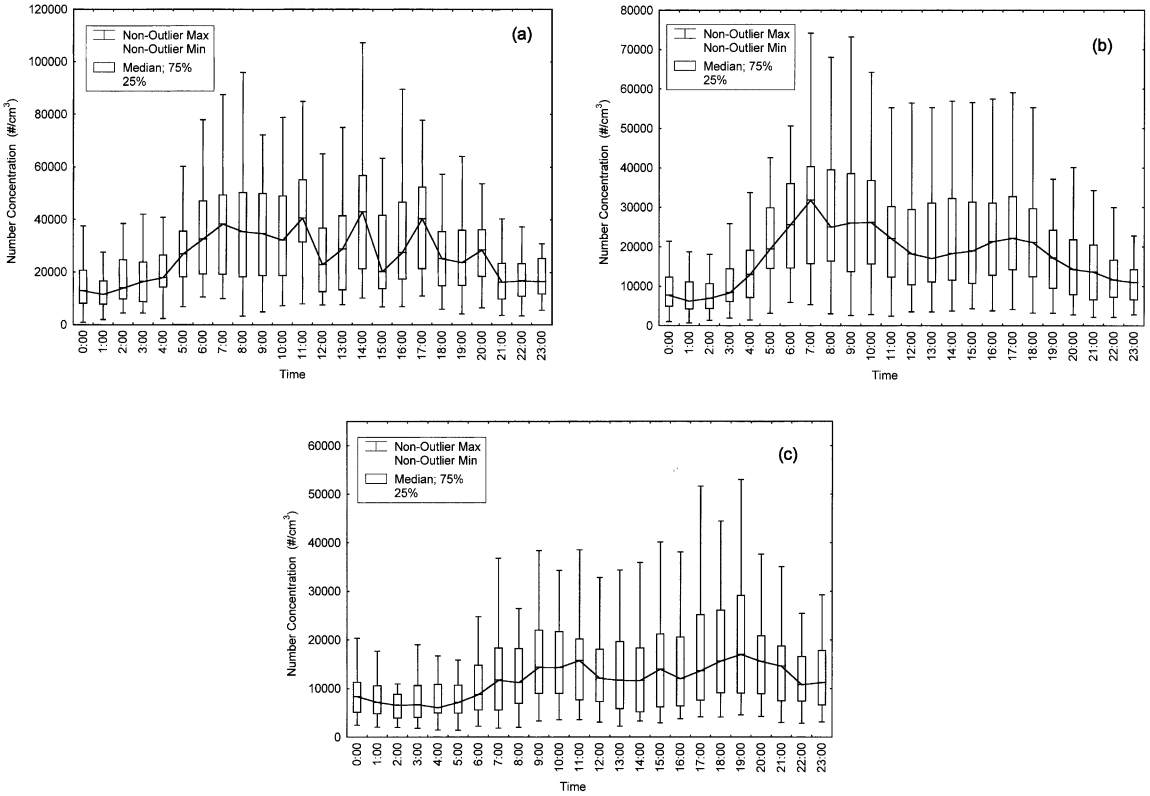

Fig. 2. Diurnal variation of total (a), ultrafine (b) and accumulation (c) number concentration on weekdays in Erfurt.

better correlated with accumulation particles. PCA also identified a similar behaviour in all three cities, indicating two major components responsible for 58–63% of the variance in the parameters measured. According to PCA results two common sources of variation appear to be related to airborne pollutants and two to meteorological parameters. Airborne pollutants are divided into two major source categories, one identified with particle number concentrations and the other related to mass-based information. Our findings suggest that in the cities

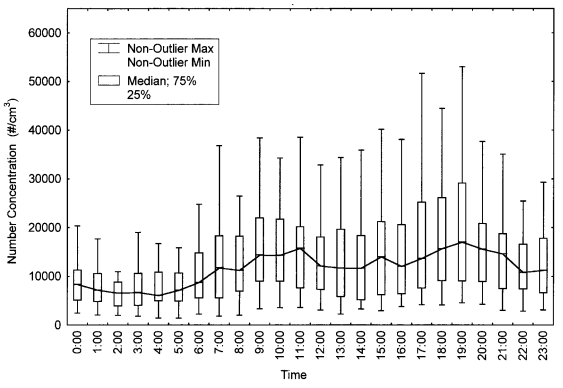

Fig. 3. Diurnal variation of ultrafine particles on weekends in Erfurt.

studied there are two emission source categories, one for ultrafine particles and the other for coarse particles (in our case smaller than 2.5 μm), and that these categories behave differently. However, we have earlier shown that in other cities the correlation between ultrafine and coarse particles can be high (Pekkanen et al., 1997). Our findings, therefore, suggest that it is important in epidemiological studies to investigate number and mass concentrations separately.

The division of the meteorological parameters into major components was not so clear. Wind speed had a negative association with the number concentrations of ultrafine particles, especially in Helsinki. High wind speed may be responsible for the effective dispersal of ultrafine particles in the city area, whereas temperature and relative humidity had little effect. The negative association between wind speed and ultrafine particles in Helsinki indicates that sources like traffic close to the monitoring site may have more effect on measured number concentrations in Helsinki than in Erfurt and Alkmaar, where the concentrations may be already more dispersed before entering the monitoring site. Highest hourly averages of particles were up to 188,000 cm^{-3}. Highest levels were observed during weekdays. The differences between daily and hourly averages were small but the hourly peak values were 2.5–4 times higher than the daily maximums. The coefficients of variation were also higher for hourly concentrations than for daily ones, which implies a high diurnal variability in number concentrations of ultrafine and accumulation particles. The clear profile in hourly average ultrafine particle concentrations on weekdays, due to human activities, is similar to that found in Pasadena near Los Angeles, USA (Hughes et al., 1998). $PM_{2.5}$ concentrations have also been found to have pronounced diurnal variations in some locations (Harrison et al., 1997). However, little diurnal variability was observed in the accumulation fraction in the present study.

Exposure assessment is an important component of epidemiological studies, where the emphasis is to establish exposure–response relationships. For more accurate exposure assessment, it is important to take into account the diurnal variation in the concentration of particles, as it has been shown (Gold et al., 2000) that health effects may be determined by more immediate exposure to particles than the past 24 h. An estimate of the number of deposited particles as a dose received by the lungs can be calculated using a lung deposition model based on the lung deposition of particles of different sizes, activity level of the subject and the ambient particle size distribution (Voutilainen et al., 2000). The hourly total dose of particles in the alveolar region can vary from less than 10^9 to more than 10^{10} particles h^{-1}, indicating that exposure of the population to ultrafine particles can vary greatly as a function of the time of the day.

5. Conclusions

Total, ultrafine and accumulation number concentrations, as well as mass concentration of $PM_{2.5}$ particles and blackness of $PM_{2.5}$ filters related to Black Smoke were simultaneously monitored in three European cities over the winter period of three months and a half. The results showed statistically significant differences in the 24 h averages of $PM_{2.5}$ and the blackness of the $PM_{2.5}$ filters between the cities, but not in number concentrations of ultrafine particles. Total number concentrations differed statistically significantly between Helsinki and the other cities, but not between Erfurt and Alkmaar.

In addition to size, ultrafine and $PM_{2.5}$ particles differ in their sources and temporal variability in urban air. Number concentrations of ultrafine particles and mass concentrations of $PM_{2.5}$ particles in the same city are poorly correlated. Also, the marked diurnal variation in ultrafine particles suggest that the 24 h time resolution used today is not sufficient for exact evaluation of exposure. According to principal component analysis airborne particulate pollutants seem to be divided into two categories, one identified with particle number concentrations and the other related to mass-based information. The present results underline the importance of using both particle number and mass concentrations to evaluate urban air quality.

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